

# PATENT ABSTRACTS OF JAPAN

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## (54) CURABLE COMPOSITION

### (57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject composition, improved in hard and brittle properties and weather resistance or the like while retaining the adhesion of an epoxy resin and useful especially as an elastic adhesive by including a specific vinylic monomer having a crosslinkable silyl group and an epoxy resin therein.

SOLUTION: This composition is obtained by mixing (A) a vinylic polymer, having at least one crosslinkable silyl group represented by the formula  $[\text{Si}(\text{R}_1)_2-\text{b}(\text{Y})\text{bO}]_m-\text{Si}(\text{R}_2)_3-\text{a}(\text{Y})_a$  [R1 and R2 are each a 1-20C alkyl, a 7-20C aryl or the like; Y is OH or the like; (a) is 0, 1, 2 or 3; (b) is 0, 1 or 2; (m) is an integer of 0-19, with the proviso that  $[(a)+mb] \geq 1$ ] having preferably <1.8 ratio of the weight-average molecular weight to the number-average molecular weight, especially an acrylic or a methacrylic polymer with (B) an epoxy resin, especially a bisphenol A type epoxy resin at a mixing ratio of the components A/B within the range of (100/1) to (1/100) expressed in terms of weight ratio.

## \* NOTICES \*

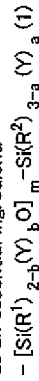
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## CLAIMS

[Claim(s)]

[Claim 1] The following two ingredients: A vinyl system polymer which has at least one crosslinkable silyl groups shown by (I) general formula (1), a hardenability constituent which uses a (II) epoxy resin as an essential ingredient.



[Each of R<sup>1</sup> and R<sup>2</sup> among a formula An alkyl group of the carbon numbers 1-20, An aryl group of the carbon numbers 6-20, an aralkyl group of the carbon numbers 7-20, or (R')<sub>3</sub>SiO - (R' is a univalent hydrocarbon group of the carbon numbers 1-20, and) three R' being the same and differing --- \*\*\*\* - when the Tori ORGANO siloxy group shown is shown and R<sup>1</sup> or two or more R<sup>2</sup> exist, they may be the same and may differ. When Y shows a hydroxyl group or a hydrolytic basis and two or more Y exists, they may be the same and may differ. a shows 0, 1, 2, or 3, and b shows 0, 1, or 2, m is an integer of 0-19. However, it shall satisfy that it is a+mb>=1.]

[Claim 2] (I) The hardenability constituent according to claim 1 whose ratio of weight average molecular weight and a number average molecular weight which were measured with gel permeation chromatography of a vinyl system polymer of an ingredient is less than 1.8.

[Claim 3] (I) A vinyl system polymer of an ingredient is a hardenability constituent given in any 1 paragraph among claims 1-2 which are acrylic (meta) polymers.

[Claim 4] (I) It is a hardenability constituent given in any 1 paragraph among claims 1-3, wherein a manufacturing method of a vinyl system polymer of an ingredient is a living-radical-polymerization method.

[Claim 5] (I) It is a hardenability constituent given in any 1 paragraph among claims 1-4, wherein a manufacturing method of a vinyl system polymer of an ingredient is the atomic move RAJIRARU polymerizing method.

[Claim 6] (I) It is a hardenability constituent given in any 1 paragraph among claims 1-5 which have the crosslinkable silyl groups shown by a general formula (1) of an ingredient in at least one molecular chain terminals.

[Claim 7] (I) A process: (1) organic halogenated compound of the following [polymer / which has at least one crosslinkable silyl groups shown by a general formula (1) of an ingredient / vinyl system ], Or a vinyl system polymer which has halogen at the end by using a sulfonyl halide compound as an initiator and carrying out the radical polymerization of the vinyl system monomer by making a transition metal complex into a catalyst is manufactured, (2) By making a oxy anion which has an alkenyl group react, and replacing halogen. It is a hardenability constituent given in any 1 paragraph among claims 1-6 which are the polymers obtained by; to which a hydrosilane compound which has the crosslinkable silyl groups which manufactures a vinyl system polymer which has an alkenyl group at the end, and is shown by (3) general formulas (1) is made to react.

[Claim 8] (I) By polymerizing by a living-radical-polymerization method, a vinyl system polymer which has the crosslinkable silyl groups shown by a general formula (1) of an ingredient the following process: (1) vinyl system monomers, Manufacture a vinyl system polymer and a vinyl system polymer which has an alkenyl group at the end by making a compound which (2) Continues and has at least two low alkenyl groups of polymerization nature react is manufactured, It is a hardenability constituent given in any 1 paragraph among claims 1-6 which are the polymers obtained by; changed into a silyl group content substituent by making a hydrosilane compound which has the crosslinkable

silyl groups which shows an end alkenyl group by the general formula 1 react.  
[Claim 9] (I) An epoxy resin of an ingredient is a hardenability constituent given in any 1 paragraph among claims 1-8 which are bisphenol A type epoxy resins.  
[Claim 10] Elastic adhesives using a hardenability constituent given in any 1 paragraph among claims 1-9.

[Translation done.]

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the hardenability constituent by which refining was carried out with the vinyl system polymer which has at least one crosslinkable silyl groups. While sticking firmly to various substrates by blending to an epoxy resin in more detail after hardening, it has elastic character and is related with a hardenability constituent useful especially as elastic adhesives.

[0002]

[Description of the Prior Art] Epoxy resin adhesive is used in the wide range industrial fields, such as a car, a vehicle, an airplane, shipbuilding, electronics, construction, and engineering works, from the reliability over the outstanding adhesive strength and endurance to wide range materials, such as metal, a plastic, wood, glass, ceramics, a stone, and concrete. However, since [that an elastic modulus is high] energy absorbing capacity is low, the hardened material generally has a hard and weak fault. For this reason, it has left the problem to adhesion of material which a coefficient of linear expansion is large and is different, and adhesion of a member which receives displacement repeatedly by a thermo cycle like a building material.

[0003] In order to solve this problem — an epoxy resin — crosslinkable silyl groups — even if small, what is called modified silicone system elastic adhesives that blended the polyether system polymer which it has one piece are used widely.

[0004]

[Problem(s) to be Solved by the Invention] However, the elastic adhesives by the above-mentioned epoxy resin and the blend of a polyether system polymer have various problems. First, an epoxy resin and the polyether system polymer which has crosslinkable silyl groups have bad compatibility. Usually, although the soft elastic body of the structure in which the epoxy resin carried out micro-disperse into the matrix of a polyether polymer is obtained, the thing of the hard type which the polyether polymer distributed in the epoxy matrix conversely cannot be obtained. A polyether system polymer has the problem that it cannot be used in the field as which weatherability and heat resistance are generally required from having the 3rd class hydrogen group in main chain structure.

[0005] In order to solve these points, three element systems of the epoxy-polyether (meta) acrylic acrylic polymer with sufficient compatibility with an epoxy resin as a third component are proposed (JP 2-214759 A). However, since the acrylic polymer used here (meta) is compounded by the free radical polymerization, molecular weight distribution is hyperviscosity widely and there is a problem that a mixture with an epoxy resin will also be hyperviscosity. Since crosslinkable silyl groups cannot be introduced by a high ratio, there is also a problem that the elastic character obtained with much trouble will be spoiled, by blending a polyether system polymer.

[0006] Therefore, in this invention, while improving the hard and weak character, maintaining the adhesive strength of an epoxy resin, a weatherproof level is also improved and let it be SUBJECT to provide the hypoviscosity hardenability constituent which gives the broad elastic body from hard to elasticity further.

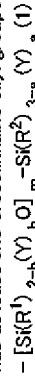
[0007]

[Means for Solving the Problem] By using a hardenability constituent which uses as an essential ingredient a vinyl system polymer which has at least one crosslinkable silyl groups, and an epoxy

resin, it found out that an aforementioned problem was solved and this invention was reached.

[0008]

[Embodiment of the Invention] The vinyl system polymer of the (1) ingredient used in this invention has at least one crosslinkable silyl groups shown with a following general formula (1).



[Each of R<sup>1</sup> and R<sup>2</sup> among a formula The alkyl group of the carbon numbers 1-20, The aryl group of the carbon numbers 6-20, the aralkyl group of the carbon numbers 7-20, or (R<sup>1</sup>)<sub>3</sub>SiO — (R<sup>1</sup>) is a univalent hydrocarbon group of the carbon numbers 1-20, and) three R<sup>1</sup> being the same and differing — \*\*\*\* — when the Tori ORGANO siloxy group shown is shown and R<sup>1</sup> or two or more R<sup>2</sup> exist, they may be the same and may differ. When Y shows a hydroxyl group or a hydrolytic basis and two or more Y exists, they may be the same and may differ. a shows 0, 1, 2, or 3, and b shows 0, 1, or 2. m is an integer of 0-19. However, it shall satisfy that it is a+mb>1.]

Especially as a hydrolytic basis shown by the above-mentioned Y, it is not limited, but can use a publicly known thing conventionally, and specifically, The point of hydrogen, a halogen atom, an alkoxy group, an acyloxy group, a KETOKISHI mate group, an amino group, an amide group, an aminooxy group, a sulfinyl group, an alkenyloxy group, etc. being mentioned, and hydrolysis nature being mild and being easy to deal with it to especially an alkoxy group is preferred. This hydrolytic basis and a hydroxyl group can be combined with one silicon atom in the 1-3 ranges, and total of a+mb, i.e., a hydrolytic basis, has the preferred range of 1-5. When a hydrolytic basis and a hydroxyl group join together in [two or more] a cross-linking silicon group, they may be the same or may differ. The number of the silicon atoms which constitute a cross-linking silicon compound may be one, and although it may be two or more pieces, there may be a case of the silicon atom connected by the siloxane bond to about 20 pieces.

[0009] As a monomer which constitutes the main chain of the vinyl system polymer which has at least one crosslinkable silyl groups of a general formula (1), there are no restrictions in particular and various kinds of things can be used. Especially as a vinyl system monomer used for manufacture of the main chain of the vinyl system polymer of this invention, it is not limited but various kinds of things can be used. If it illustrates, acrylic acid (meta), methyl acrylate (meta), (Meta) Ethyl acrylate, acrylic acid (meta)-n-propyl, acrylic acid (meta) isopropyl, (Meta) Acrylic acid-n-n-butyl, isobutyl acrylate (meta), (Meta) Acrylic acid-tert-butyl, acrylic acid (meta)-n-pentyl, (Meta) Acrylic acid-n-hexyl, acrylic acid (meta) cyclohexyl, (Meta) Acrylic acid-n-heptyl, acrylic acid (meta)-n-octyl, (Meta) Acrylic acid-2-ethylhexyl, acrylic acid (meta) nonyl, (Meta) Decyl acrylate, acrylic acid (meta) dodecyl, acrylic acid (meta) phenyl, (Meta) Acrylic acid toluyl, acrylic acid (meta) benzyl, acrylic acid (meta)-2-methoxy ethyl, (Meta) Acrylic acid-3-methoxy propyl, acrylic acid (meta)-2-hydroxyethyl, (Meta) Acrylic acid-2-hydroxypropyl, acrylic acid (meta) stearyl, metaglycidyl acrylate (meta), acrylic acid (meta) 2-aminoethyl, gamma-(methacryloyl oxypropyl) trimethoxysilane, the ethyleneoxide addition of acrylic acid (meta), (Meta) Acrylic acid trifluoromethyl methyl, an acrylic acid (meta) 2-trifluoro methylethyl, (Meta) Acrylic acid 2-perfluoro ethylethyl, acrylic acid (meta)-2-perfluoro ethyl-2-perfluoro butylethyl, (Meta) Acrylic acid 2-perfluoro ethyl, acrylic acid (meta) perfluoro methyl, (Meta) Acrylic acid JIPA, fluoromethylmethyl, acrylic acid (meta) 2-perfluoro methyl-2-perfluoro ethylmethyl, (Meta) Acrylic acid 2-perfluoro hexylethyl, acrylic acid (meta) 2-perfluoro decylethyl, (Meta) Acrylic acid series (meta) monomers, such as acrylic acid 2-perfluoro hexadecylethyl, Styrene, Styrene system monomers, such as vinyltoluene, alpha-methylstyrene, KURORU styrene, styrene sulfonic acid, and its salt; Perfluoro ethylene, Monoalkyl ester and dialkyl ester of silicon content vinyl system monomer, maleic anhydrides, such as fluoride content vinyl monomer, vinyltrimethoxysilane, such as perfluoro propylene and vinylidene fluoride, and vinyltriethoxysilane, maleic acid, and maleic acid; Fumaric acid, Monoalkyl ester and dialkyl ester of fumaric acid; Maleimide, Methylmaleimide, ethylmaleimide, propyl maleimide, butylmaleimide, Hexylmaleimide, octylmaleimide, dodecylmaleimide, stearyl maleimide, Maleimide system monomers, such as phenylmaleimide and cyclohexylmaleimide; Acrylonitrile, Nitrile group content vinyl system monomers, such as a methacrylonitrile; Acrylamide, Amide group content vinyl system monomers, such as methacrylamide; Vinyl acetate, Conjugated dienes, such as alkenes; butadiene, such as vinyl ester; ethylene, such as vinyl propionate, vinyl pivalate, benzoic acid vinyl, and vinyl cinnamic acid, and propylene, and isoprene; VCM/PVC, a vinylidene chloride, an allyl chloride, allyl alcohol, etc. are mentioned. These may be used

independently, and even if it carries out copolymerization of the plurality, they are not cared about. Acrylic acid (meta) expresses acrylic acid and/or methacrylic acid with the above-mentioned expressive form.

[0010] The acrylic (meta) polymer obtained by compounding the crosslinkable silyl groups of a general formula (1) in the above-mentioned monomer with the vinyl system polymer which it has at least one piece, using an acrylic acid series (meta) monomer 40% of the weight or more is more preferred from a physical-properties side. Although there is no restriction in particular about the molecular weight of the vinyl system polymer which has at least one crosslinkable silyl groups, it is preferred that it is in the range of 500–100,000. The original characteristic of a vinyl system polymer is it hard to be revealed that a molecular weight is 500 or less, and handling becomes it difficult that it is 100,000 or more.

[001] There is no restriction in particular about the ratio ( $M_w/M_n$ ) of the weight average molecular weight ( $M_w$ ) and the number average molecular weight ( $M_n$ ) which measured crosslinkable silyl groups according to the molecular weight distribution of the vinyl system polymer which it has at least one piece, i.e., gel permeation chromatography. However, in order easily and to acquire hardened material physical properties sufficient moreover, the molecular weight distribution of narrow one is preferred. [ by stopping low the viscosity at the time of considering it as a hardenability constituent ] It is 1.3 or less still more preferably 1.4 or less still more preferably 1.5 or less still more preferably 1.6 or less still more preferably 1.7 or less more preferably [ as a value of molecular weight distribution, less than 1.8 are preferred, and ]:

[0012] The vinyl system polymer which has at least one crosslinkable silyl groups can be obtained by the various polymerizing methods, and the method in particular is not limited. By however, the point of the flexibility of a monomer, and the ease of control to a radical polymerization method. The vinyl system polymer which has a specific functional group which can introduce crosslinkable silyl groups directly or can be changed into crosslinkable silyl groups at one step or several steps of reactions is obtained. The method of obtaining the vinyl system polymer which has at least one crosslinkable silyl groups is more preferred by changing this specific functional group into crosslinkable silyl groups.

[0013] The radical polymerization method used in the method of compounding the vinyl system polymer which has a specific functional group containing crosslinkable silyl groups, it can classify into the "control radical polymerization method", which can introduce a specific functional group into "the general radical polymerization method" to which copolymerization of the monomer which has a specific functional group, and the vinyl system monomer is only carried out, and to carry out, and the position by which the end etc. were controlled using an azo compound, a peroxide, etc. as a polymerization initiator. "A general radical polymerization method" is a simple method, and it is [method] usable also in this invention. However, since the monomer which has a specific functional group in this method is not introduced into a probable polymer, when it is going to obtain a polymer with a high rate of organic-functions-izing, It is necessary to use this monomer quite in large quantities, and there is a problem that the rate of a polymer that this specific functional group is not introduced becomes large, by use in small quantities conversely. Since it is a free radical polymerization, the problem that only a large polymer with high viscosity is obtained also has molecular weight distribution.

[0014]A "control radical polymerization method" further, By polymerizing using the chain transfer agent which has a specific functional group. It can classify into the "living-radical-polymerization method" the polymer of the molecular weight as a design is obtained mostly, by growing without the "chain transfer agent method" the vinyl system polymer which has a functional group at the end is obtained and a polymerization growth end causing a termination reaction etc.

[0005] Although the "chain transfer agent method" can obtain a polymer with a high rate of organic-functionalizing and it is usable also in this invention, the chain transfer agent which has quite a lot of specific functional groups to an initiator is required, and there is a problem on the financial side also including processing. Like the above-mentioned "general radical polymerization method", since it is a free radical polymerization, the problem that only the polymer whose viscosity is large and is high is obtained also has molecular weight distribution. Unlike these polymerizing methods, a "living-radical-polymerization method". Since a rate of polymerization is high, and the termination reaction by radical coupling etc. occurs easily, though it is a radical polymerization made difficult [ control ]. While a termination reaction does not occur easily and the narrow polymer ( $M_w/M_n$  is 1: to about 1.5) of

molecular weight distribution is obtained, a molecular weight is freely controllable by the preparation ratio of a monomer and an initiator.

[0016] Therefore, since the monomer which can obtain a polymer with molecular weight distribution narrow [ a "living-radical-polymerization method" ] and low viscosity, and also has a specific functional group can be introduced into the almost arbitrary positions of a polymer, As a manufacturing method of the vinyl system polymer which has the above-mentioned specific functional group, it is more desirable. Although living polymerization means the polymerization in which an end always continues having activity and the chain grows in the narrow sense, the pseudo-living polymerization which grows while that by which the end was inactivated, and the activated thing are generally in an equilibrium situation is also included. The definition in this invention is also the latter.

[0017]As for the "living-radical-polymerization method", research is positively made into various groups in recent years. As the example, for example A Journal of American chemical society (J. Am.Chem.Soc.), 1994, 116 volumes, the thing using a cobalt porphyrin complex as shown in 7943 pages, Macro leakage-at-bulb KYURUZU (Macromolecules), 1994, The thing using radical scavengers, such as a nitroxide compound as shown in 27 volumes and 7228 pages, The "atom transfer radical polymerization" (Atom Transfer Radical Polymerization:ATRP) etc. which uses an organic halogenated compound etc. as an initiator and makes a transition metal complex a catalyst is raised.

[20018]Also in a "living-radical-polymerization method", an organic halogenated compound or a sulfonyl halide compound An initiator, The "atom-transfer-radical-polymerization method" which polymerizes a vinyl system monomer by making a transition metal complex into a catalyst, As a manufacturing method of the vinyl system polymer which in addition to the feature of the above-mentioned "living-radical-polymerization method" has halogen comparatively advantageous to a functional group conversion etc. at the end, and has a specific functional group from the flexibility of a design of an initiator or a catalyst being large, it is still more desirable. As this atom-transfer-radical-polymerization method, Matyjaszewski et al. [ for example, ], Journal OBU American chemical society (J. Am.Chem.Soc.) 1995, 117 volumes, 5614 pages, macro leakage-at-bulb KYURUZU (Macromolecules) 1995, 28 volumes, 7901 pages, science (Science) 1996, 272 volumes, 28 volumes, 1721 pages, etc. will be mentioned in 866 pages, WO 96/No. 30421 gazette, WO 97/No. 18247 gazette or Sawamoto et al., and macro leakage-at-bulb KYURUZU (Macromolecules) 1995, 1995.

[0019] The organic halogenated compound which has an organic halogenated compound, especially a reactant high carbon-halogen bond in this atom transfer radical polymerization. (For example, the carbonyl compound which has halogen in an alpha position and the compound which has halogen in a benzylic position), or a sulfonyl halide compound is used as an initiator. As a transition metal complex used as a catalyst of the above-mentioned atom transfer radical polymerization, the complex used as a central metal can use the 7th fellows of the periodic table, eight fellows, nine fellows, ten fellows, and 11 group elements. As a desirable thing, the complex of zerovalent copper, univalent copper, a divalent ruthenium, divalent iron, or divalent nickel is mentioned. Especially, a copper complex is preferred. If a univalent copper compound is illustrated concretely, they will be a cuprous chloride, the first copper of bromination, a cuprous iodide, a cuprous cyanide, copper I oxide, the first copper of perchloric acid, etc. When using a copper compound, in order to improve catalytic activity 2,2'-bipyridyl and its derivative, Ligands, such as polyamine, such as a 1,10-phenanthroline and its derivative, tetramethylethylenediamine, pentamethyl diethylenetriamine, and hexamethyl tris(2-aminoethyl) amine, are added. The tris(phenyl phosphine) complex ( $\text{RuCl}_2(\text{PPh}_3)_3$ ) of divalent ruthenium chloride is also preferred as a catalyst. When using a ruthenium compound as a catalyst, aluminum alkoxides are added as an activator. The screw triphenyl phosphine complex of divalent iron ( $\text{FeCl}_2(\text{PPh}_3)_2$ ). The screw triphenyl phosphine complex ( $\text{NiCl}_2(\text{PPh}_3)_2$ ) of divalent nickel and the screw tributyl phosphine complex ( $\text{NiBr}_2(\text{PBu}_3)_2$ ) of divalent nickel are also preferred as a catalyst.

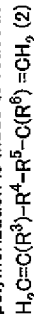
[0020]As a monomer of a vinyl system used in this polymerization, there are no restrictions in particular and all the already illustrated things can be used conveniently. The above-mentioned polymerization reaction can be performed in a non-solvent or various kinds of solvents. As a solvent, for example hydrocarbon system solvent; diethylether, such as benzene and toluene, Ether system solvents, such as a tetrahydrofuran; Halogenated hydrocarbon system solvent; acetone, such as a methylene chloride and chloroform; Ketone solvent, such as methyl ethyl ketone and methyl isobutyl

ketone; Methanol, Ethanol, propanol, n-butyl alcohol, Alcoholic solvent, such as tert-butyl alcohol; carbonate system solvents, such as ester solvent; ethylene carbonate, such as nitrile system solvent; ethyl acetate, such as acetonitrile, propionitrile, and benzonitrile, and butyl acetate, and propylene carbonate, etc. are mentioned. These can be independent, or can mix two or more sorts, and can be used. The above-mentioned polymerization can be performed in 0-200 \*\*, and it is the range of room temperature -150 \*\* preferably.

[0021] Although the vinyl system polymer which has at least one crosslinkable silyl groups shown by the general formula 1 can be obtained using the method of illustrating below, it is not necessarily limited to these. As a synthesizing method of the vinyl system polymer which it has at least one piece, crosslinkable silyl groups, (A) The hydrosilane compound which has crosslinkable silyl groups in the vinyl system polymer which has at least one alkenyl group. By the method (C) radical polymerization which makes the compound which has in a monad a basis which can react to crosslinkable silyl groups and a hydroxyl group like an isocyanate group react to the vinyl system polymer which has at least one method (B) hydroxyl group made to add under hydrosilylation catalyst existence. When compounding a vinyl system polymer by the method (D) radical polymerization to which the compound it has a compound, and the alkenyl group and crosslinkable silyl groups of polymerization nature in one molecule is made to react when compounding a vinyl system polymer, Method; etc. to which the compound which has stable carbanion with crosslinkable silyl groups in one molecule in the vinyl system polymer which has at least one high carbon-halogen bond of method (E) reactivity which uses the chain transfer agent which has crosslinkable silyl groups is made to react are raised.

[0022] The vinyl system polymer which has at least one alkenyl group used by the method of (A) is obtained by various methods. Although a synthesizing method is illustrated below, it is not necessarily limited to these.

(A-a) A method to which the compound it has a compound and an alkenyl group of polymerization nature and a low alkenyl group of polymerization nature in a monad which is mentioned, for example to the following general formula (2) when compounding a vinyl system polymer by a radical polymerization is made to react as the 2nd monomer.

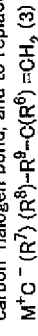


(R<sup>3</sup> shows hydrogen or a methyl group among a formula, R<sup>4</sup> shows -C(O) O- or O-, m-, and p-phenylene group, and R<sup>5</sup> may show theivalent organic group of direct coupling or the carbon numbers 1-20, and may include one or more ether bonds.) R<sup>6</sup> shows hydrogen or the alkyl group of the carbon numbers 1-10, the aryl group of the carbon numbers 6-10, or the aralkyl group of the carbon numbers 7-10.

Although there is no restriction at the stage to which the compound it has a compound and an alkenyl group of polymerization nature and a low alkenyl group of polymerization nature in a monad is made to react, it is especially living radical polymerization. When it expects rubber character, it is preferred to make it react as the 2nd monomer after the telophase of a polymerization reaction or the ending reaction of a predetermined monomer.

[0023] (A-b) When compounding a vinyl system polymer by living radical polymerization, A method to which the compound which has at least two low alkenyl groups of polymerization nature, such as 1,5-hexadiene, 1,7-octadiene, and 1,9-decadiene, for example is made to react after the telophase of a polymerization reaction, or the ending reaction of a predetermined monomer.

(A-c) How to make various kinds of organic metallic compounds which have an alkenyl group like organic tin, such as allyl tributyl tin and allyl trioctyl tin, for example react to the vinyl system polymer which has at least one reactant high carbon-halogen bond, and to replace halogen by it. [0024] (A-d) How to make the stabilization carbanion which has an alkenyl group which is mentioned to a general formula (3) react to the vinyl system polymer which has at least one reactant high carbon-halogen bond, and to replace halogen by it.



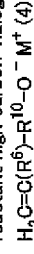
inside of formula, and R<sup>6</sup> --- the above --- the same --- both R<sup>7</sup> and R<sup>8</sup> are electron withdrawing groups which stabilize carbanion C<sup>-</sup>, or, in one side, another side shows hydrogen, the alkyl group of the carbon numbers 1-10, or a phenyl group by said electron withdrawing group. R<sup>9</sup> may show the

divalent organic group of direct coupling or the carbon numbers 1-10, and may include one or more ether bonds. M<sup>+</sup> shows alkali metal ion or the 4th class ammonium ion.

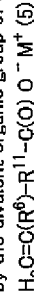
As an electron withdrawing group of R<sup>7</sup> and R<sup>8</sup>, especially the thing that has the structure of -CO<sub>2</sub>R, -C(O)R, and -CN is preferred.

[0025] (A-e) To the vinyl system polymer which has at least one reactant high carbon-halogen bond. For example, make the metal simple substance or organic metallic compound like zinc act, and a eno rate anion is prepared. How to make after an appropriate time react to the electrophilicity compound which has alkenyl groups, such as an alkenyl group content compound which has a leaving group like halogen or an acetyl group, a carbonyl compound which has an alkenyl group, an isocyanate compound which has an alkenyl group, and acid halide which has an alkenyl group.

[0026] (A-f) How to make the oxy anion or carboxylate anion which has an alkenyl group as shown, for example in the general formula (4) or (5) react to the vinyl system polymer which has at least one reactant high carbon-halogen bond, and to replace halogen by it.



(R<sup>6</sup> and M<sup>+</sup> are the same as the above among a formula.) R<sup>10</sup> may include one or more ether bonds by the divalent organic group of the carbon numbers 1-20.



(R<sup>6</sup> and M<sup>+</sup> are the same as the above among a formula.) It is mentioned that R<sup>11</sup> may include one or more ether bonds by the divalent organic group of direct coupling or the carbon numbers 1-20 etc. [0027] The synthetic method of the vinyl system polymer which has at least one above-mentioned reactant high carbon-halogen bond as an example, (E-a) a carbon tetrachloride as shown in JP,4-132706 A in a radical polymerization, ethylene chloride, carbon tetrabromide, and a methylene bromide --- how (chain transfer agent method) to use a halogenide [like ] for a chain transfer agent.

[0028] (E-b) The above organic halogenated compounds etc. are used as an initiator, and although atom-transfer-radical-polymerization method; etc. which make a transition metal complex a catalyst are mentioned, it is not necessarily limited to these. Although the vinyl system polymer which has at least one alkenyl group is possible also for obtaining from the vinyl system polymer which has at least one hydroxyl group and can use the method of illustrating below, it is not necessarily limited to these. How to make a base like sodium methoxide (A-g) act on the hydroxyl group of the vinyl system polymer which has at least one hydroxyl group, and make it react to an alkenyl group content halogenide like an allyl chloride.

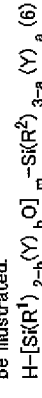
[0029] (A-h) A method to which alkenyl group content isocyanate compounds, such as an allylisocyanate, are made to react

(A-i) A method (meta) to which alkenyl group content acid halide like acrylic acidchloride is made to react under base existence, such as pyridine.

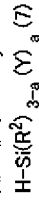
(A-j) Method; etc. which make alkenyl group content carboxylic acid, such as acrylic acid, react under existence of an acid catalyst are mentioned.

[0030] When halogen does not participate in the method of introducing an alkenyl group like this invention (A-a) (A-b) directly, it is preferred to compound a vinyl system polymer using a living-radical-polymerization method. The method of the point that control is easier to (A-b) is still more preferred. When introducing an alkenyl group by changing halogen of the vinyl system polymer which has at least one reactant high carbon-halogen bond. The organic halogenated compound which has at least one reactant high carbon-halogen bond. Or it is preferred to use the vinyl system polymer which is obtained by using a sulfonyl halide compound as an initiator and carrying out the radical polymerization of the vinyl system monomer by making a transition metal complex into a catalyst (atom-transfer-radical-polymerization method) and which has at least one reactant high carbon-halogen bond at the end. The method of the point that control is easier to (A-f) is still more preferred.

[0031] Although there is no restriction in particular as a hydrosilane compound which has crosslinkable silyl groups, if a typical thing is shown, the compound shown by a general formula (6) will be illustrated.



(R<sup>1</sup>, R<sup>2</sup>, a, b, m, and Y are the same as the above among a formula.)  
Also in these hydrosilane compound, it is especially a general formula (7).

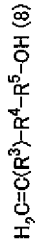


the compound which has a cross-linking group shown by (the inside of a formula, R<sup>2</sup>, Y, and a are the same as the above) — acquisition — it is desirable from an easy point.

[0032]When making the hydrosilane compound which has the above-mentioned crosslinkable silyl groups add to an alkenyl group, a transition metal catalyst is usually used. The thing which, for example, made carriers, such as a platinum simple substance, alumina, silica, and carbon black, distribute a platinum solid as a transition metal catalyst, A complex with chloroplatinic acid, chloroplatinic acid, alcohol, aldehyde, ketone, etc., a platinum-olefin complex, and a platinum (0)-divinyl tetramethyl disiloxane complex are mentioned. As an example of catalysts other than a platinum compound, RhCl(PPh<sub>3</sub>)<sub>3</sub>, RhCl<sub>3</sub>, RuCl<sub>3</sub>, FeCl<sub>3</sub>, AlCl<sub>3</sub>, PdCl<sub>2</sub>-H<sub>2</sub>O, NiCl<sub>2</sub>, TiCl<sub>4</sub>, etc. are mentioned.

[0033](B) And the manufacturing method of the vinyl system polymer which has at least one hydroxyl group used by the method of (A-g) - (A-j) is not limited to these methods, although the following methods are illustrated.

(B-a) A method to which the compound it has a compound, and the alkenyl group and hydroxyl group of polymerization nature in a monad polymer is mentioned, for example to the following general formula (8) when compounding a vinyl system polymer by a radical polymerization is made to react as the 2nd monomer.



(The inside of a formula, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup> are the same as the above)

Although there is no restriction at the stage to which the compound it has a compound, and the alkenyl group and hydroxyl group of polymerization nature in a monad is made to react, it is especially living radical polymerization, and when it expects rubber character, it is preferred to make it react as the 2nd monomer after the telophase of a polymerization reaction or the ending reaction of a predetermined monomer.

[0034](B-b) A method to which 10-UNDESE Norian, 5-hexenol, and alkenyl alcohol like allyl alcohol are made to react after the telophase of a polymerization reaction, or the ending reaction of a predetermined monomer for example when compounding a vinyl system polymer by living radical polymerization.

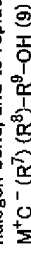
(B-c) For example, the method of carrying out the radical polymerization of the vinyl system monomer, using so much a hydroxyl group content chain transfer agent like the hydroxyl group content polysulfide shown in JP.5-262808.A.

(B-d) For example, the method of carrying out the radical polymerization of the vinyl system monomer using hydrogen peroxide or a hydroxyl group content initiator as shown in JP.6-239912.A and JP.8-283310.A.

(B-e) For example, the method of carrying out the radical polymerization of the vinyl system monomer, using alcohols as shown in JP.6-116312.A superfluously.

(B-f) For example, the method of introducing a hydroxyl group into an end by making halogen of the vinyl system polymer which has a reactant high carbon-halogen bond in at least one piece react to hydrolysis or hydroxyl group-containing compound by a method as shown in JP.4-132706.A etc.

(B-g) How to make the stabilization carbanion which has a hydroxyl group which is mentioned to a general formula (9) react to the vinyl system polymer which has at least one reactant high carbon-halogen bond, and to replace halogen by it.

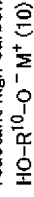


(It is the same as the inside of a formula, and R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup> and \*\*\*\*\*)

As an electron withdrawing group of R<sup>7</sup> and R<sup>8</sup>, especially the thing that has the structure of -CO<sub>2</sub>R, -C(O)R, and -CN is preferred.

[0035](B-h) How to, make the metal simple substance or organic metallic compound like zinc act on the vinyl system polymer which has at least one reactant high carbon-halogen bond for example, to prepare a eno rate anion, and to make aldehyde or ketone react to after an appropriate time.

(B-i) How to make the oxy anion or carboxylate anion which has a hydroxyl group as shown, for example in the general formula (10) or (11) react to the vinyl system polymer which has at least one reactant high carbon-halogen bond, and to replace halogen by it.



(The inside of a formula, R<sup>10</sup>, and M<sup>+</sup> are the same as the above)



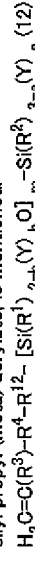
(The inside of a formula, R<sup>11</sup>, and M<sup>+</sup> are the same as the above)

\*\* is mentioned.

[0036]When halogen does not participate in the method of introducing a hydroxyl group like (B-a) - (B-e) in this invention directly, it is preferred to compound a vinyl system polymer using a living-radical-polymerization method. The method of of the point that control is easier to (B-b) is still more preferred. When introducing a hydroxyl group by changing halogen of the vinyl system polymer which has at least one reactant high carbon-halogen bond, Obtain by using an organic halogenated compound or a sulfonyl halide compound as an initiator, and carrying out the radical polymerization of the vinyl system monomer by making a transition metal complex into a catalyst (atom-transfer-radical-polymerization method). It is preferred to use for an end the vinyl system polymer which has at least one reactant high carbon-halogen bond. The method of of the point that control is easier to (B-i) is still more preferred.

[0037]As a compound which has in a monad a basis which can react to crosslinkable silyl groups and a hydroxyl group like an isocyanate group. For example, gamma-isocyanate propyltrimethoxysilane, gamma-isocyanate propylmethyl dimethoxysilane, gamma-isocyanate propyl triethoxysilane, etc. are mentioned, and the catalyst of a urethane-sized reaction generally known as occasion demands can be used.

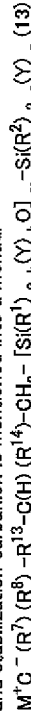
[0038]As a compound it has a compound, and the alkenyl group and crosslinkable silyl groups of polymerization nature in the monad used by the method of (C). For example, what is shown with following general formulas (12), such as trimethoxysilylpropyl (meta) acrylate and methyl dimethoxy silyl propyl (meta) acrylate, is mentioned.



(R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, Y, a, b, and m are the same as the above among a formula.) R<sup>12</sup> may include one or more ether bonds by the divalent organic group of direct coupling or the carbon numbers 1-20.

Especially although there is no restriction in particular at the stage to which the compound it has a compound, and the alkenyl group and crosslinkable silyl groups of polymerization nature in a monad is made to react, it is living radical polymerization. When it expects rubber character, it is preferred to make it react as the 2nd monomer after the telophase of a polymerization reaction or the ending reaction of a predetermined monomer. The hydrosilane etc. which have the mercaptan which has crosslinkable silyl groups and crosslinkable silyl groups which are used by the chain transfer agent method of (D), and which are shown in JP.3-14068.B and JP.4-55444.B as a chain transfer agent which has crosslinkable silyl groups are mentioned.

[0039]The vinyl system polymer which is used by the method of (E) and which has at least one reactant high carbon-halogen bond can be obtained by the method of (E-a) - (E-b) as above-mentioned. What is shown by a general formula (13) as a compound having crosslinkable silyl groups and stabilization carbanion is mentioned into a monad.



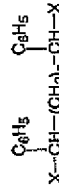
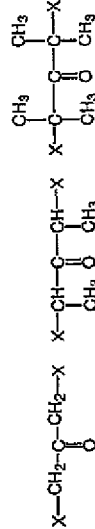
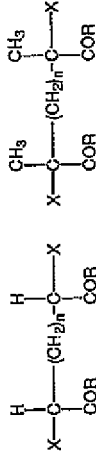
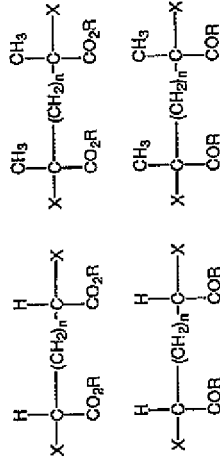
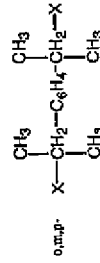
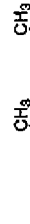
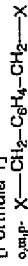
(It is the same as R<sup>1</sup>, R<sup>2</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, a, b, m, and \*\*\*\*\* among a formula.) R<sup>14</sup> in which R<sup>13</sup> may include one or more ether bonds by the divalent organic group of direct coupling or the carbon numbers 1-10 shows hydrogen or the alkyl group of the carbon numbers 1-10, the aryl group of the carbon numbers 6-10, or the aralkyl group of the carbon numbers 7-10.

As an electron withdrawing group of R<sup>7</sup> and R<sup>8</sup>, especially the thing that has the structure of -CO<sub>2</sub>R, -C(O)R, and -CN is preferred.

[0040]The vinyl system polymer which crosslinkable silyl groups has at the end of an at least one-piece chain. In order to obtain an organic halogenated compound or a sulfonyl halide compound by the polymerizing method using an initiator and a transition metal complex as a catalyst, it is preferred to

use as an initiator the organic halogenated compound which has two or more reactant high carbon-halogen bonds used as the starting point, or a sulfonyl halide compound. As those examples, [0041]

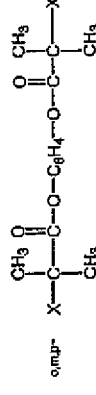
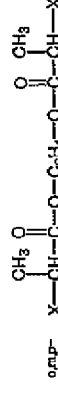
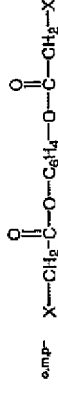
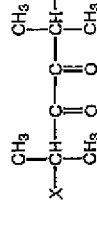
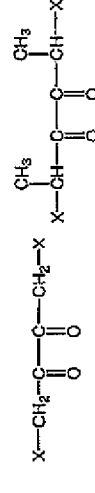
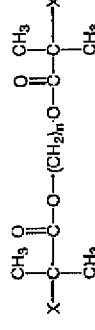
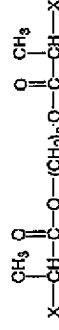
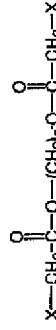
[Formula 1]



[0042](R expresses an alkyl group of the carbon numbers 1-20, the carbon number 6-20 aryl groups or the carbon number 7-20 aralkyl groups among a formula.)  $\text{C}_6\text{H}_4$  expresses a phenylene group. n expresses an integer of 0-20. X expresses chlorine, bromine, or iodine.

[0043]

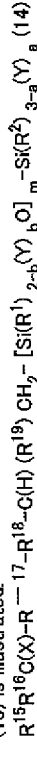
[Formula 2]



[0044](X expresses chlorine, bromine, or iodine among a formula.) n expresses the integer of 0-20.  $\text{C}_6\text{H}_4$  expresses a phenylene group. etc. — it is raised. Besides the above, the vinyl system polymer which has crosslinkable silyl groups at the end of an at least one-piece chain can be obtained.

[0045]If the organic halogenated compound which has crosslinkable silyl groups is used as an initiator, the vinyl system polymer which has crosslinkable silyl groups in one end and in which other ends have the structure of the general formula 2 will be obtained. Thus, if halogen of the stop end of the polymer obtained is changed into a crosslinkable-silyl-groups content substituent, the vinyl system polymer which has crosslinkable silyl groups in both ends can be obtained. The already indicated method can be used as the converting method.

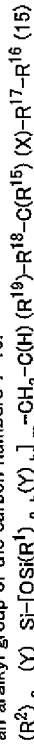
[0046]Although there is no restriction in particular as an organic halogenated compound which has crosslinkable silyl groups, what has the structure shown, for example in the general formula (14) and (15) is illustrated



( $\text{R}^1$ ,  $\text{R}^2$ , a, b, m, X, and Y are the same as the above among a formula.) Independently  $\text{R}^{15}$  and  $\text{R}^{16}$  Hydrogen or an alkyl group of the carbon numbers 1-20. An aryl group of the carbon numbers 6-20, an aralkyl group of the carbon numbers 7-20 or a thing mutually connected in the other end, and  $\text{R}^{17}$  show  $-\text{C}(\text{O})-\text{O}-$ ,  $-\text{C}(\text{O})-$  or  $-\text{O}-$ ,  $m-$ , and  $p$ -phenylene group.  $\text{R}^{19}$  in which  $\text{R}^{18}$  may include one or more ether bonds by a divalent organic group of direct coupling or the carbon numbers 1-10 shows hydrogen or an alkyl group of the carbon numbers 1-10, an aryl group of the carbon numbers 6-10, or



an aralkyl group of the carbon numbers 7-10.



(The inside of a formula,  $R^1, R^2, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, a, b, m, X$ , and  $Y$  are the same as the above) If an organic halogenated compound which has crosslinkable silyl groups is used as an initiator, a polymer whose one end is crosslinkable silyl groups and in which other ends are halogen will be obtained, but, A vinyl system polymer which has crosslinkable silyl groups in both ends can be obtained also by carrying out coupling of the halogen ends using a compound which can replace halogen of this polymer and which has a total of two or more same or different functional groups.

[0047] Although there is no restriction in particular as a compound which can replace end halogen and which has a total of two or more same or different functional groups, polyol, polyamine, polycarboxylic acid, polythiol and those salts, an alkaline metal sulfide, etc. are preferred. If an organic halogenated compound which has an alkenyl group is used for an initiator, it will have an alkenyl group in one end, and a polymer in which other ends are halogen will be obtained. Thus, if halogen of an end of a polymer obtained is changed into an alkenyl content substituent, if a vinyl system polymer which has an alkenyl group in both ends can be obtained and this alkenyl group is changed into crosslinkable silyl groups by an above-mentioned method etc., a vinyl system polymer which has crosslinkable silyl groups in both ends can be obtained.

[0048] In this use as which rubber character is required, since a molecular weight between the points constructing a bridge which has big influence on rubber elasticity can take greatly, as for at least one of crosslinkable silyl groups, it is preferred that it is in an end of a chain, and it is still more preferred that it is in molecular chain terminals altogether. Therefore, as for a vinyl system polymer which is used when compounding a vinyl system polymer which at least one crosslinkable silyl groups has and which has a hydroxyl group, halogen, or at least one alkenyl group, it is preferred that these functional groups are what exists in an end of a chain.

[0049] Although a vinyl system polymer which has at least one crosslinkable silyl groups, and a method of manufacturing an acrylic polymer especially (meta) are indicated by JP.3-14068B, JP.4-55444B, JP.6-211922A, etc., for example, Since these methods use a "chain transfer agent method", such crosslinkable silyl groups exists in an end at a comparatively high rate, but there is a problem that molecular weight distribution of a polymer obtained is generally as large as two or more, and viscosity becomes high. Therefore, it is preferred to use a living-radical-polymerization method for obtaining a vinyl system polymer with low viscosity with narrow molecular weight distribution which has crosslinkable silyl groups at the end at a high rate.

[0050] As an epoxy resin which is a (ID) ingredient in this invention, A bisphenol A type epoxy resin, bisphenol F type epoxy resin, Novolak type epoxy resin, a glycidyl ether type epoxy resin of a bisphenol A propylene oxide addition, Fire retardancy type epoxy resins, such as a hydrogenation bisphenol A type epoxy resin and glycidyl ether of tetrabromobisphenol A, p-oxybenzoic acid glycidyl ether ester typed epoxy resin, m-aminophenol type epoxy resin, A diaminodiphenylmethane system epoxy resin, a urethane modified epoxy resin, Various cycloaliphatic-epoxy-resin and N,N-diglycidyl triglycidyl isocyanurate, polyalkylene glycol diglycidyl ether, glycidyl ether of polyhydric alcohol like glycerin, a hydantoin type epoxy resin, and petroleum resin, etc. are illustrated, Not a thing limited to these but an epoxy resin currently generally used may be used.

[0051] Reactivity is [ what has an epoxy group in / at least one / a monad also in these epoxy resins ] high when hardening, and a hardened material is preferred from points — it is easy to make three-dimensional meshes of a net. Bisphenol A type epoxy resins and novolak type epoxy resin are specifically more preferred, and bisphenol A type epoxy resins are still more preferred. These epoxy resins can be independent, or can mix two or more sorts, and can be used.

[0052] If various hardening agents of an epoxy resin are used together, an effect may show up further, and concomitant use of various hardening agents is also included by this invention. If such a hardening agent is illustrated, ethylenediamine, diethylenetriamine, Triethylenetetramine, tetraethylenepentamine, hexamethylenediamine, Diethylamino propylamine, N-aminoethyl piperazine, Lamy Ron C-280 by BASF A.G., Araldit HY-904 by CIBA, MENSENJI amine by Iom and HASU, Isophoronediamine, diaminoxyhexamethane, m-xylenediamine, The 1st class amine, such as m-phenylenediamine, diaminodiphenylmethane, and diaminodiphenyl sulfone,  $(OH)_3$  Straight-chain-shape

diamine shown by  $2N(CH_2)_nN(CH_3)_2$  (the inside n of a formula is an integer of 1-10),  $(CH_3)_3$  Straight chain tertiary amine shown by  $2-(N(CH_2)_n-CH_3)$  (the inside n of a formula is an integer of 0-10),

Tetramethyl guanidine, the 3rd class of alkyl monoamine shown by  $N(CH_2)_nCH_3)_3$  (the inside n of a formula is an integer of 1-10), Triethanolamine, piperidine, NN'-dimethylpiperazine, Triethylenediamine, pyridine, piperidine, diazabicycloundecene, benzyltrimethylamine, The 2nd class or tertiary amine, such as 2-(dimethyl aminomethyl) phenol and 2,4,6-tris(dimethyl aminomethyl) phenol,

Acid anhydrides, such as phthalic anhydride, trimellitic anhydride, pyromellitic dianhydride, and anhydrous benzophenone tetracarboxylic acid, Various polyamide resin, dicyandiamide and its derivative, various imidazole derivatives, Ketimine etc. which are obtained by a condensation reaction of a compound, an amine compound, and a carbonyl compound which have an amino group and a hydroxyl silyl group are mentioned into monads, such as N-(beta-aminoethyl)-gamma-aminopropyl trimethoxysilane. JP.7-242737A etc. are mentioned as an example of a ketimine compound.

[0053] Since intensity will improve more if a compound which has a basis in which a reaction is possible in both crosslinkable silyl groups shown in this hardenability resin composition by a general formula (1) and an epoxy group is added, it is desirable. As the example, N-(beta-aminoethyl)-gamma-aminopropyl trimethoxysilane, N-(beta-aminoethyl)-gamma-aminopropyl triethoxysilane, gamma-glycidioxypropyltrimethoxysilane, etc. are mentioned, for example.

[0054] In a hardenability constituent of this invention, although the mixture ratio of a vinyl system polymer which has at least one crosslinkable silyl groups of a (I) ingredient, and an epoxy resin of a (II) ingredient has the preferred range of  $100 / 1 - 1 / 100$  at a weight ratio, it is still more preferred that it is in the ranges of  $100 / 5 - 5 / 100$ . As for this hardenability constituent, it is still more preferred to use as elastic adhesives used for adhesion of material in which coefficients of linear expansion differ, and adhesion of a member which receives displacement repeatedly by a thermo cycle.

[0055] Even if it uses a condensation catalyst in stiffening a vinyl system polymer which has at least one crosslinkable silyl groups of this invention, it is not necessary to carry out. As a condensation catalyst, titanate, dibutyltin dilaurate, such as tetrabutyl titanate and tetrapropyl titanate, Dibutyl tin diacetyl acetonate, dibutyltin maleate, dibutyltin diacetate, Dibutyl tin dimethoxide, dibutyltin oxide, carboxylate, carboxylic acid, or a reactant of hydroxyl group-containing compound, Organic tin compounds, such as tin octylate and naphthenic acid tin; Aluminum tris acetylacetonate,

Organoaluminum compounds, such as aluminumtrisethoxyacetate and diisopropoxy aluminum ethylacetate; Zirconium tetra acetylacetonate zirconium TETRAISOPROPOKSAIDO, Organic zirconium compounds, such as zirconium tetra butoxide; Organic-lead-compounds [ such as lead octylate, ], A butylamine, octylamine, dibutyl amine, monoethanolamine, Diethanolamine, triethanolamine, diethylenetriamine, triethylenetetramine, oleylamine, octylamine, cyclohexylamine, benzylamine, diethylamino propylamine, xylene diamine, triethylenediamine, guanidine, Diphenylguanidine, 2,4,6-tris(dimethyl aminomethyl) phenol, Morpholine, N-methylmorpholine, 1, 3-diazabicyclo (5, 4, 6) An amine compound of undecene 7 grade, Or those carboxylate; a reactant of lauryl amine and tin octylate or a reactant of an amine compound and an organic tin compound like a mixture, and mixture; — low-molecular-weight-polyamide resin; obtained from superfluous polyamine and polybasic acid — superfluous polyamine and a resultant, amino group of an epoxy compound. What is necessary is just to use one sort of silanol catalysts, or two sorts or more with publicly known a silane coupling agent which it has, for example, gamma-aminopropyl trimethoxysilane, N-(beta-aminoethyl) aminopropyl methyl dimethoxysilane, etc. if needed. As for the amount used, it is preferred to carry out 0-10 weight-section use to vinyl system polymer 100 weight section which has at least one crosslinkable silyl groups. When an alkoxy group is used as the hydrolytic basis Y, it is preferred to use a curing catalyst only with this polymer, since the cure rate is slow.

[0056] A filler can be added in order to adjust the mechanical physical property of a hardenability constituent of this invention. Specifically Fumed silica, sedimentation nature silica, a silicic acid anhydride, hydrous silicic acids, and reinforcing filler, calcium carbonate like carbon black, Fillers, such as magnesium carbonate, diatomite, calcination clay, clay, talc, titanium oxide, bentonite, organic bentonite, ferric oxide, a zinc oxide, an active white, and a melt balloon; asbestos, glass fiber, and a fibrous filler like a filament can be used. To obtain a hardened material with high intensity with these fillers. Mainly Fumed silica, sedimentation nature silica, a silicic acid anhydride, hydrous silicic acids,



carbon black. A desirable result will be obtained if a filler chosen from surface treatment detailed calcium carbonate, calcination clay, clay, an active white, etc. is added in the range of one to 200 weight section to vinyl system polymer 100 weight section which has at least one crosslinkable silyl groups. When elongation wants to obtain a hardened material which is size with low strength, A desirable result will be obtained if a filler mainly chosen from titanium oxide, calcium carbonate, talc, ferric oxide, a zinc oxide, a mill balloon, etc. is added in the range of one to 200 weight section to vinyl system polymer 100 weight section which has at least one crosslinkable silyl groups. These fillers may be used by one kind and may carry out two or more kind mixing use.

[0057]A plasticizer can be added for adjustment of physical properties and viscosity. Specifically Dibutyl phthalate, diheptylphthalate, di(2-ethylhexyl) phthalate, Phthalic ester, such as di-isodecyl phthalate and butylbenzyl phthalate; Dioctyl adipate, Non-aromatic dibasic acid esters, such as dioctyl sebacate; Diethylene glycol dibenzoate, Ester species of polyalkylene glycols, such as TORIECHIRENGURIKORUJIBENZOETO; Trioresyl phosphate, Phosphoric ester, such as tributyl phosphate; Poly ERLEN glycol, polyether, which changed polypropylene glycols or these hydroxyl groups — chloroparaffin, — hydrocarbon system oils, such as alkyl diphenyl and partially—hydrogenated terphenyl, etc. are mentioned — these — independence — or, although two or more sorts can use it, mixing. It does not necessarily need. These plasticizers can also be blended at the time of polymer manufacture. An adhesion promoter with which a desirable result will be obtained if the amount of plasticizers is added in the range of zero to 100 weight section to vinyl system polymer 100 weight section which has at least one crosslinkable silyl groups. The polymer by this invention itself has an adhesive property to ceramics other than glass and glass, metal, etc., or. Since it is possible to make it paste up to a wide range material by using various primers, it is not necessarily required, but it is preferred to use in order to acquire a stable adhesive property over various adherends.

[0058]As an adhesion promoter, phenol, cresol, a xyleneol, resorcinol, alkylphenol and denaturation phenol (for example, cashew oil denaturation phenol.) tall oil denaturation phenol etc. — etc. — a phenol system compound and formalin. A resol type obtained by a reaction with aldehyde system compounds, such as paraformaldehyde, or novolac type phenol resin; sulfur; A bisphenol A type epoxy resin, Bisphenol F type epoxy resin, novolak type epoxy resin, a glycidyl ether type epoxy resin of a bisphenol A propylene oxide addition, Epoxy resins, such as a hydrogenation bisphenol A type epoxy resin; Alkyl titanate, such as tetrabutyl titanate. Aromatic polyisocyanate; gamma-aminopropyl trimethoxysilane, such as tolylene diisocyanate and diphenylmethane diisocyanate, gamma-aminopropyl triethoxysilane, gamma-aminopropyl methyl dimethoxysilane, N-(beta-aminoethyl)-gamma-aminopropyl triethoxysilane, N-(beta-aminoethyl)-gamma-aminopropyl triethoxysilane. A compound which carries out a crosslinkable-silyl-groups owner to an amino group into monads, such as N-(beta-aminoethyl)-gamma-aminopropyl methyl dimethoxysilane; Gamma-glycidoxypropyltriethoxysilane, Compound; gamma-mercaptopropyltriethoxysilane which carries out a crosslinkable-silyl-groups owner to an epoxy group into monads, such as gamma-glycidoxypropyltriethoxysilane and gamma-glycidoxypropyl methyl dimethoxysilane, Compound; gamma-mercaptopropyltriethoxysilane which carries out a crosslinkable-silyl-groups owner to a sulfhydryl group into monads, such as gamma-mercaptopropyl triethoxysilane and gamma-mercaptopropylmethyl dimethoxysilane, gamma-isocyanate propyl triethoxysilane, A compound which carries out a crosslinkable-silyl-groups owner to an isocyanate group into monads, such as gamma-isocyanate propylmethyl dimethoxysilane; A compound which carries out a crosslinkable-silyl-groups owner to an amino group into the above monads, and a compound which carries out a crosslinkable-silyl-groups owner to an epoxy group into a monad. Or a reactant of a compound which carries out a crosslinkable-silyl-groups owner to an isocyanate group into a monad; gamma-(meta)acryloxypropyltriethoxysilane, gamma-(meta)acryloxypropyltriethoxysilane, Reactant [ of a compound which carries out a crosslinkable-silyl-groups owner to an acryloxy (meta) group, and a compound which carries out a crosslinkable-silyl-groups owner to an amino group into the above monads ]; etc. are mentioned into monads, such as gamma-(meta)acryloxypropylmethyl dimethoxysilane. These may be used alone or may be used together two or more kinds. A compound which carries out a crosslinkable-silyl-groups owner to an amino group especially into physical properties and a monad in which adhesive control is comparatively easy, A compound which carries out a crosslinkable-silyl-groups owner to an epoxy group into a monad, a compound

which carries out a crosslinkable-silyl-groups owner to a sulfhydryl group into a monad, A reactant of a compound which carries out a crosslinkable-silyl-groups owner to an amino group into a monad, and a compound which carries out a crosslinkable-silyl-groups owner to an epoxy group into a monad. A compound which has an organic group which has at least one of nitrogen, oxygen, and sulfur atoms, and crosslinkable silyl groups in monads, such as a reactant etc. of a compound which carries out a crosslinkable-silyl-groups owner to an acryloxy (meta) group into a monad, and a compound which carries out a crosslinkable-silyl-groups owner to an amino group into a monad, is preferred. A compound in which the above-mentioned nitrogen, oxygen, and an organic group that has at least one of sulfur atoms have an organic group which is a basis generated when an amino group, an isocyanate group, or these react, and which has a nitrogen atom in a monad, and crosslinkable silyl groups from adhesive height is still more preferred.

[0059]As for the above-mentioned adhesion promoter, it is preferred that 20 weight sections are used from 0.01 to vinyl system polymer 100 weight section which has at least one crosslinkable silyl groups. In 0.01 weight sections, it is hard to reveal an adhesive improvement effect, and has an adverse effect on the physical properties of 20 weight-section \*\*\*\*\* hardened material. An addition of an adhesion promoter is 0.5 to 5 weight section still more preferably 0.1 to 10 weight section preferably.

[0060]In order to raise hardness when stiffening a hardenability constituent, or to lower hardness, to take out elongation and to control physical properties, a physical-properties regulator can be used. As a physical-properties regulator, for example, methyl trimethoxysilane, dimethyldimethoxysilane, Alkyl alkoxysilane, such as trimethylmethoxysilane and n-propyltrimethoxysilane; Dimethyl diisopropoxysilane, Alkyl isopropoxysilane, such as methyl TORISO propenoxysilane and gamma-glycidoxy propylmethyl JISO propenoxysilane; Vinyltrimethoxysilane; Various silane coupling agents, such as vinylmethyldimethoxysilane, and silicone varnishes; polysiloxanes are added if needed. Vinyl system polymer 100 weight section [ for ] which has at least one crosslinkable silyl groups, if it adds in the range of zero to 20 weight section, a desirable result will be obtained.

[0061]In order to speed up or delay a cure rate of a hardenability constituent and to suppress thickening under storage for a hardenability regulator again, a storage stability improving agent can be added. As a hardenability regulator or a storage stability improving agent, Alcohols; methyl orthoformate NADONO ortho ester, such as methanol and ethanol; carboxylic acid, such as compound 2-ethylhexanoic acid which carries out a crosslinkable-silyl-groups owner, such as a tetraethoxysilane, methyl trimethoxysilane, and vinyltrimethoxysilane, is mentioned. Vinyl system polymer 100 weight section [ for ] which has at least one crosslinkable silyl groups, if it adds in the range of zero to 20 weight section, a desirable result will be obtained.

[0062]In addition to this, a hardenability constituent of this invention Various solvent; several-kinds silane coupling agents, such as toluene and methyl ethyl ketone, Various denaturing agents, such as a polysiloxane which has crosslinkable silyl groups; A polyamide wax, Colorant, such as the surface characteristic of rheology characteristic regulator, ultraviolet curing nature resin, such as hydrogeneration castor oil and metallic soap, oxygen hardening resin, etc. and/or weatherproof improving agent, paints, and a color; additive agents, such as an antiaging agent, an ultraviolet ray absorbent, a SadamMitsuyasu-sized agent, and a flameproofing agent, may also be used arbitrarily. A hardenability constituent of this invention can also be prepared as one component type hardened by carrying out combination seal preservation of all the combination ingredients beforehand, and absorbing hygroscopic surface moisture in the after-construction air. A vinyl system polymer which has at least one crosslinkable silyl groups, the curing catalyst and an epoxy resin, its hardening agent, or a curing catalyst is blended with according to, respectively, and it is also possible to adjust as a multicomponent type mixed before use. A liquid which uses as the main ingredients a hardening agent or a curing catalyst of a vinyl system polymer and an epoxy resin which furthermore has at least one crosslinkable silyl groups, B liquid which uses as the main ingredients a curing catalyst of a vinyl system polymer which has an epoxy resin and at least one crosslinkable silyl groups is blended with according to, respectively, and it is also possible to prepare as two component types mixed before use. Handling is easy and one component type also with few mistakes at the time of construction is more preferred. Although this invention is explained based on an example below, it is not limited to the following example.

(Synthetic example 1)

In poly (acrylic acid-n-butyl) 50 ml of composition flask which has halogen at the end, the first copper 0.63g (4.4mmol) of bromination, 0.76 g (4.4mmol) of pentamethyl diethylenetriamine, After teaching 5 ml of acetonitrile, 1.6 g (4.4mmol) of 2,5-dibromo diethyl adipate, and 44.7 g (349mmol) of butyl acrylate and performing freezing deaeration, 70 \*\* was made to react under a nitrogen atmosphere for 7 hours. A polymer which has Br basis at the end was obtained by carrying out removal refining of the copper catalyst through a column of activated alumina. Number average molecular weights of an obtained polymer were 10700 and molecular weight distribution 1.15 in GPC measurement (mobile phase chloroform, polystyrene conversion).

Under a poly (acrylic acid-n-butyl) synthetic nitrogen atmosphere which has an alkenyl group at the end, 35 g of poly (acrylic acid-n-butyl) which has halogen, the pentene acid potassium 2.2g (16.1mmol), and DMAc35mL were taught to an end obtained above, and it was made to react to a 200-ml flask at 70 \*\* for 4 hours. Water extraction refining removed unreacted pentene acid potassium and generated potassium bromide in reaction mixed liquor, and a polymer which has an alkenyl group at the end was obtained. Number average molecular weights of an obtained polymer were 11300 and molecular weight distribution 1.12 in GPC measurement (mobile phase chloroform, polystyrene conversion). The number of an alkenyl group per one molecule of polymers for which it asked from <sup>1</sup>H-NMR analysis was 1.82 pieces.

The polymer 15g which has an alkenyl group at the end obtained above to a poly (acrylic acid-n-butyl) synthetic 200mL resisting pressure coil which has crosslinkable silyl groups at the end. Taught methyl dimethoxysilane 1.8mL (14.5mmol) methyl orthoformate 0.26mL (2.4mmol) and platinum bis (divinyl tetramethyl disiloxane)10<sup>-4</sup>mmol, it was made to react at 100 \*\* for 4 hours, and a polymer which has crosslinkable silyl groups at the end was obtained. Viscosity of an obtained polymer was 44 Pa-s, and number average molecular weights were 11900 and molecular weight distribution 1.12 in GPC measurement (mobile phase chloroform, polystyrene conversion). The number of a cross-linking silicon group per one molecule of polymers was 1.46 pieces by <sup>1</sup>H-NMR analysis.

(Reference example 1)  
To polymer 100 weight section which has crosslinkable silyl groups at the end obtained in the example 1 of physical-properties measurement composition of a polymer hardened material of the synthetic example 1, dibutyltin diacetyl acetate 1 weight section was mixed, and it slushed into a mold, and deformed at a room temperature using a vacuum drier. A uniform rubber-like hardened material sheet was obtained by carrying out heat cure at 50 \*\* for 20 hours. A gel fraction for which it asked by toluene extraction was 95%, piercing 2 (1/3) item type dumbbell specimen from a rubber-like hardened material sheet, and pulling using an autograph — an examination after fracture — having carried out (200 mm/min) — time — breaking strength — 0.26MPa and elongation after fracture — 84% — it was.

(Example 1 of comparison composition)  
400 g of poly (acrylic acid-n-butyl) synthetic toluene which has the crosslinkable silyl groups using a cross-linking silicon group content monomer, it polymerized at 105 \*\* for 7 hours, carrying out nitrogen bubbling of 385 g of butyl acrylate, 15 g of methyl methacrylate dimethoxy silyl propyl, and 6 g of the azobisisobutyronitrile in 1L flask. Poly (acrylic acid-n-butyl) which has crosslinkable silyl groups was obtained by distilling off toluene. Viscosity of this polymer was 74 Pa-s, by GPC measurement (mobile phase chloroform, polystyrene conversion), a number average molecular weight was 8500 and molecular weight distribution was 2.47. The number of a hydroxyl group of an average per one molecule of polymers for which it asked from <sup>1</sup>H-NMR analysis was 1.40 pieces.

(Comparison reference example 1)  
To polymer 100 weight section which has crosslinkable silyl groups at the end obtained in the example 1 of physical-properties measurement composition of a polymer hardened material of the synthetic example 1 of comparison composition, dibutyltin diacetyl acetate 1 weight section was mixed, and it slushed into a mold, and deformed at a room temperature using a vacuum drier. A uniform rubber-like hardened material sheet was obtained by carrying out heat cure at 50 \*\* for 20 hours. A gel fraction for which it asked by toluene extraction was 78%, piercing 2 (1/3) item type dumbbell specimen from a rubber-like hardened material sheet, and pulling using an autograph — an examination — having carried out (200 mm/min) — time — breaking strength — 0.14MPa and elongation after fracture — 69% — it was.

(Example 2 of comparison composition)  
The hexacyanocobalt acid zinc-glyme complex 0.04g, a THF solution of 2.0 g of dipropylene glycol, and 9.6 g of propylene oxide were added to synthetic autoclave of hydroxyl group end polypropylene oxide, and it was made to react to it at 76 \*\* under a nitrogen atmosphere. 145.2 g of propylene oxide was added to the system of reaction after that. An unreacted monomer and a solvent were collected and refined and 150 g of oily matters were obtained. Output showed a single peak by GPC analysis, and molecular weight distribution (Mw/Mn) was 1.14. The hydroxyl value was 11.8 mgKOH/g.

Decompression devolatilization was carried out, after adding 5.8 g (30.2mmol) of methanol solution (28wt%) of sodium methoxide to 120 g of hydroxyl group end polypropylene oxide obtained by the synthetic above of unsaturation group end polypropylene oxide and making it react at 130 \*\* in autoclave for 1 hour. It returned under a nitrogen atmosphere, the allyl chloride 2.8g (36.2mmol) was added, and it was made to react for 2 hours. This reaction mixture was dissolved in hexane, and after carrying out adsorption treatment with aluminum silicate, unsaturation group end polypropylene oxide was obtained by carrying out decompression distilling off of the hexane. 120 g of unsaturation group end polypropylene oxide obtained by composition of the synthetic above of crosslinkable-silyl-groups end polypropylene oxide is taught to resisting pressure glass reaction vessels, it stirred for 30 minutes after adding 0.02 g of isopropanol solutions (what dissolved H<sub>2</sub>, 25-g PtCl<sub>6</sub> and 6H<sub>2</sub>O in 500 g of isopropanol) of chloroplatinic acid. 2.1 g (20.2mmol) of methyl dimethoxysilane was dropped, and it was made to react at 90 \*\* for 2 hours. By decompressing, volatile matter content was removed and crosslinkable-silyl-groups end polypropylene oxide was obtained. Viscosity of this polymer was 6 Pa-s, by GPC measurement (mobile phase chloroform, polystyrene conversion), a number average molecular weight was 17300 and molecular weight distribution was 1.14.

(Example 1) Poly (acrylic acid-n-butyl) and Epicoat 828 (a bisphenol A type epoxy resin, a product made from oil recovery shell epoxy) which have crosslinkable silyl groups at the end obtained in the synthetic example 1 were mixed by the weight ratios 2:1 and 1:1, centrifugal deforming was carried out, and a bubble was extracted. A situation of mixed liquor was observed seven days after settlement, and compatibility was judged. A result was shown in Table 1.

(Comparative examples 1 and 2) A polymer obtained in the examples 1 and 2 of comparison composition instead of a polymer obtained in the synthetic example 1 was used, and also compatibility was judged like Example 1. A result was united with Table 1 and shown.

[0063]  
[Table 1]

用いた重合体 (重合比)	実施例1 合成例1		比較例1 比較合成例1		比較例2 比較合成例2	
	重合体:エポコート828	2:1	分離濁りなし	分離濁りなし	分離濁りなし	分離濁りあり
		1:1	分離濁りなし	分離濁りなし		

[0064]By 1:1 of what is dissolved, it has separated into two phases and Example 1 and the comparative example 1 understand 2:1 that the compatibility of a vinyl system polymer and an epoxy resin is high for a polyether system polymer of the comparative example 2, while a vinyl system polymer and an epoxy resin were dissolving any system.

(Example 2) Epicoat 828 to vinyl system polymer 100 weight section obtained in the synthetic example 1 50 weight sections, The amount part of silanol condensation catalyst (#918, product made from Sankyo organicity) duplexes, and 2,4,6-tris(dimethyl aminomethyl) phenol Five weight sections, The amount part of N-(beta-aminoethyl)-gamma-aminopropyl trimethoxysilane duplexes and water 1 weight section were mixed, and mixed liquor was slushed into a flat tip mold after centrifugal deforming, it was recuperated at 50 \*\* with a room temperature on the 3rd on the 1st, and a sheet of a hardened material was produced. 2 (1/3) item type dumbbell specimen was pierced from a sheet of a hardened material, it examined by having pulled using an autograph, and stress (M30) measurement was carried out at the time of 30% extension (200 mm/min). It applied to an aluminum specimen of A1050P, and it was recuperated at 50 \*\* with a room temperature on the 4th on the 3rd. A hauling shear bonding strength examination was done based on JIS K6850. A result was doubled and it was shown in Table 2.

(Comparative examples 3 and 4) The polymer obtained in the examples 1 and 2 of comparison composition instead of the polymer obtained in the synthetic example 1 was used, and also physical properties were measured like Example 2. The result was doubled and it was shown in Table 2.

[0065]

[Table 2]

用いた重合体	実施例2		比較例3		比較例4	
	合成例1	比較合成例1	比較合成例1	比較合成例2	比較合成例1	比較合成例2
M30(MPa)	4. 9	1. 5	4. 6	0. 4	6. 5	6. 6
せん断強さ(MPa)	4. 9	1. 5	4. 6	0. 4	6. 5	6. 6

[0066]The shear strength of Example 2 is also high at a high modulus. The combination mixture of the comparative example 3 is hyperviscosity, and it is harder to deal with it than the thing of Example 2. The hardened materials were physical properties with them. [ a modulus, the low shear strength, or ] [ insufficient as adhesives ] Although the shear strength is enough, since the modulus is low, the deformation in jointing becomes large too much, and it is unsuitable. [ of the comparative example 4 ]

(Example 3) Epicoat 828 to vinyl system polymer 100 weight section obtained in the synthetic example 1 100 weight sections. The amount part of silanol condensation catalyst (#918, product made from Sankyo organicity) duplexes, and 2,4,6-tris(dimethyl aminomethyl) phenol Ten weight sections. The amount part of N-(beta-aminoethyl)-gamma-aminopropyl trimethoxysilane duplexes and water 1 weight section were mixed, it applied to the aluminum specimen of A1050P, and it was recuperated at 50 \*\* with the room temperature on the 4th on the 3rd. The hauling shear bonding strength examination was done based on JIS K6850. The result was shown in Table 3.

(Comparative examples 5 and 6) The polymer obtained in the examples 1 and 2 of comparison composition instead of the polymer obtained in the synthetic example 1 was used, and also physical properties were measured like Example 3. The result was doubled and it was shown in Table 3.

[0067]

[Table 3]

用いた重合体	実施例3		比較例5		比較例6	
	合成例1	比較合成例1	比較合成例1	比較合成例2	比較合成例1	比較合成例2
せん断強さ(MPa)	8. 0	5. 0	5. 0	8. 9	8. 9	8. 9

[0068]The combination mixture of the comparative example 5 is hyperviscosity, and it is harder to deal with it than the thing of Example 3. Example 3 and the comparative example 6 had sufficient intensity. However, since the comparative example 6 is a presentation which is not dissolved as the comparative example 2 showed, it is unsuitable from the point of the stable manifestation of physical properties. The intensity of the comparative example 5 is insufficient.

[Translation done.]